



The  
Patent  
Office

PC1/GB99/03439  
097830044

INVESTOR IN PEOPLE

GB 99/3439

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

REC'D 17 NOV 1999

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that by virtue of an assignment registered under the Patents Act 1977, the application is now proceeding in the name as substituted.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

**PRIORITY  
DOCUMENT**

SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed *Andrew Gentry*  
Dated 3 November 1999





The  
Patent  
Office



INVESTOR IN PEOPLE

GB9823085.7

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

DEVRO PLC  
Modiesburn  
Chryston  
GLASGOW  
G69 0JE  
United Kingdom

Incorporated in the United Kingdom

[ADP No. 07054794001]

FRAUNHOFER-GESELLSCHAFT ZUR FÖRDERUNG DER ANGEWANDTEN  
FORSCHUNG E.V.  
Leonrodstrasse 54  
80636 Munich  
Federal Republic of Germany

[ADP No. 07417058002]



220CT98 ES99204-6 C25070  
P01/7700 0.00 - 9823085.7

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)



1. Your reference

DCM/ED/P08470GB

2. Patent application number

(The Patent Office will fill in this part)

12 (1) OCT 1998

9823085.7

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Devro plc  
Moodiesburn  
Glasgow

SECTION 11(1) 1977 ACT

G69 0JE

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Scotland, United Kingdom

16.4.99

4. Title of the invention

Cellulose Film Structure

5. Name of your agent (if you have one)

Cruikshank & Fairweather  
19 Royal Exchange Square  
Glasgow G1 3AE

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it)

547002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description	15
Claim(s)	1
Abstract	
Drawing(s)	9

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents  
(please specify)

11. I/We request the grant of a patent on the basis of this application.

Signature Cruikshank & Fairweather Date 20 October 1998

12. Name and daytime telephone number of person to contact in the United Kingdom Mr D C MacDougall 0141 221 5767

## Warning

*After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.*

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.*
- Write your answers in capital letters using black ink or you may type them.*
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.*
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.*
- Once you have filled in the form you must remember to sign and date it.*
- For details of the fee and ways to pay please contact the Patent Office.*

CELLULOSE FILM STRUCTURE

The present invention relates to an extruded cellulose product having a novel structure, and a process and apparatus for the production thereof. In particular, it relates to cellulose film produced by extruding a solution of cellulose, water and an amine-oxide according to the well known amine-oxide extrusion process.

The production of extruded cellulose articles, such as fibres, sheets or tubes has been known for more than a century. In this so-called "viscose" process cellulose is derivatised with carbon disulphide and solubilised in diluted sodium hydroxide to form a solution and the solution is extruded. The extruded cellulose is then regenerated and reverts to its solid form. The viscose process has been used for the manufacture of sausage casings, flat cellophane films, rayon fibres, bottle caps etc. A disadvantage of the viscose process is that it employs carbon disulphide as an intermediate, which is environmentally undesirable.

More recently, the so-called "amine-oxide" process has been developed wherein the cellulose is dissolved in a mixture of water and an amine-oxide solvent. A commonly used amine-oxide solvent is the tertiary amine-oxide NMMO (N-methyl morpholine N-oxide). This solvent is able to dissolve cellulose without having to first derivatise the cellulose, as for example in the viscose process. Once solubilised the cellulose will precipitate from the solution as a regenerated cellulose product by contacting

the solution with a precipitation liquid which is a non-solvent for cellulose and a solvent for NMMO. The most frequently used precipitation liquid for the amine-oxide process is water. Prior to extrusion, the cellulose amine-oxide solution may be heated to a temperature of around 100°C. Thermal stabilisers, such as propylgalate, may be added to the solution to inhibit the thermal degradation of NMMO.

It has now been surprisingly found that using the amine-oxide process, extruded cellulose films having novel structure and enhanced mechanical properties may be obtained.

The present invention provides an extruded cellulose product, such as a film or fibre, having a substantially uniform distribution of fine pores throughout its cross-sections.

The fine porous structure obtained is quite distinct from the structure found in cellulose films produced according to the viscose process. In the viscose process, a cross-section through the extruded film shows a relatively few large pores and these pores tend to be elongate with an aspect ratio in excess of 5 to 1. Generally, the pores are elliptical in cross-section. In contrast, the pore structure of the cellulose films of the present invention is quite different and shows a widespread distribution of fine pores substantially evenly distributed throughout the cross-section of the film. The pores tend to be somewhat irregular in shape but the aspect ratio



tends to be less than 5 to 1 (e.g. in the range 1:1 - 1:5). This is believed to give rise to improved mechanical properties.

As determined by electronmicroscopy, the pore size of the extruded film varies dependent on whether the film has never been dried, is dried, or has been dried and rewetted. Surprisingly, the pore size tends to vary more markedly depending on these parameters than does the pore size of cellulose films produced from the conventional viscose process. In particular, it is found that the pore size of extruded never-dried cellulose film tends to lie in the region 10-500nm whereas the pore size of the dried film tends to lie in the region 5-50nm as determined by electronmicroscopy. In contrast, the spindle-like or elliptical voids of the viscose process tend to have a minor dimension of 5-150nm and a major dimension of 300-750nm.

Comparative pore dimensions have also been investigated using small angle X-ray (SAXS) techniques as described herein. It is noted that the pore volume of dried film tends to lie in the region 0.04-0.05% volume fraction (compared to 0.25 for the viscose process) the pore volume for rewetted film tends to lie in the range 0.05-2% (compared to 0.11 for viscose material). The pore dimension of dried material tends to lie in the range 2.0-2.5nm (compared to 2.4 for the viscose process) and the pore dimension for rewetted material is in the range 3.2-3.7 (compared to 2.0 for the viscose process). The pore

internal surface area of dried film lies in the range  $0.7-1.0\text{m}^2/\text{cm}^3$  (compared to  $4.3\text{m}^2/\text{cm}^3$  for the viscose process) and for rewetted film tends to be in the region  $5-25\text{m}^2/\text{cm}^3$  (compared to about 2 for the viscose process). Thus, the material of the present invention tends to exhibit a multiplicity of fine pores compared to a relatively small number of large pores in the viscose process.

It is found that there is increased permeability through the cellulose film of the present invention which is typically in the range  $225-500\text{mg } \mu\text{m ml/min cm}^2 \text{ g}$  (compared to a value of about 213 for the viscose process). The measurement methodology is given herein.

Finally, it is observed that the material of the present invention is less crystalline and exhibits a crystallinity typically in the range 35-42% (compared to the viscose process of 45%).

It is also observed that variations in the temperature of the precipitation bath (usually water or dilute NMMO solution) can lead to variations in the structure of the extruded cellulose film. In particular, higher temperatures (such as  $20^\circ\text{C}$ ) tend to favour large pore size, whereas lower temperatures (for example  $10^\circ\text{C}$ ) tend to favour smaller pore sizes.

Embodiments of the present invention will now be described by way of example only with reference to the following Example and appended Figures.

EXAMPLE

A cellulose solution for extrusion was prepared by mixing cellulose pulp with an aqueous NMMO solution containing about 50% by weight NMMO. Water was removed from the mixture by applying heat and a reduced pressure. The water boiled off at approximately 70°C and the vapours were recovered in a condenser. Once the water content had been reduced to about 12%, the NMMO monohydrate formed and the cellulose began to dissolve in the NMMO monohydrate solution. A stabiliser was added to the solution to inhibit thermal degradation of NMMO. The temperature was then increased to about 95°C and all the cellulose fibres dissolved to form an extrusion solution. The pressure was further reduced to remove air bubbles from the cellulose solution. At a temperature about 100°C, the cellulose solution is a visco-elastic melt with a high viscosity and a pronounced elastic behaviour. Time to produce the cellulose solution was about 3 hours.

The cellulose solution was then stored in a storage vessel and extruded through an annular die so as to form a NMMO-cellulose tube. The tube was passed into a precipitation bath containing a precipitation medium, such as water or aqueous NMMO solution. A positive pressure was applied into the air gap between the extrusion die and the precipitation bath so as to keep the tube inflated. The inner volume of the tube was also kept filled up with precipitation liquid, the composition of which was controlled to be constant.

Measurements were carried out on the extruded film and photomicrographs thereof are shown in Figures 1 to 8. Figure 9 is an X-ray pole figure.

#### 1. Transmission Electromicroscopy (TEM)

Transmission electromicroscopy was carried out according to well known procedures. The cross-sectional morphology of the NMMO casings is characterised by a network structure in which pores of varying size are embedded (see Figure 1). In general, the cross-sectional morphology can be divided into three zones, which do not have sharp boundaries and which tend to differ with respect to pore size and pore distribution, referred to as outer region, middle region and outer region. As a function of the processing conditions both symmetrical and asymmetrical morphologies can occur, as well as variations in dimensions of the regions and pore sizes (Table 1). It is also noted that precipitation bath temperatures have an effect on pore dimensions, lower temperatures (e.g. 10°C) giving generally smaller pores than higher temperatures (e.g. 20°C). This becomes evident by comparing Figures 1, 3 and 5 according to the present invention with Figure 10 (viscose process for comparison). Reference to Table 1 also shows a comparison of cross-sectional morphologies of never-dried samples on the one hand and dried and rewetted samples on the other, which shows that the drying process causes irreversible changes in the pore size such that rewetting is not capable of re-establishing the original pore size of

never dried samples.

The inner surface of the samples shows mainly an irregular network of aggregated fibrillar bundles without any preferred orientation (Figures 2, 4 and 6). The dimensions of the fibrillar bundles vary somewhat as a function of processing conditions, as does the surface roughness. The morphology of the viscose casings (Figures 7 and 8) by comparison is markedly different from those of the NMMO films of the present invention. Typical for the viscose casings is a symmetrical dense precipitation structure with immersed spindle-like voids, which are oriented in the machine direction of extrusion. Also, the surface structure of the viscose casings (Figure 8) is different from that of the NMMO films of the present invention. Characteristic of the viscose surfaces are micro and macro crazes as well as wrappings, preferentially oriented in the machine extrusion direction. Depending on processing conditions, variations of the pattern may occur.

## 2. X-Ray Texture Investigation

In order to determine the orientational state of the samples, pole figures were measured with an X-ray texture goniometer. The (1-10) and (110) pole figures were recorded in reflection and transmission geometries, respectively. Figure 9 shows an example of the (1-10) pole figure of Sample 14. From the half-width of the distribution curves obtained by cutting the pole figures in the machine (M) and transverse (T) directions the

parameters of uniplanar orientation in the M-direction ( $O_{gm}$ ) and in the transverse direction ( $O_{gt}$ ) and the axial chain orientation parameters ( $O_{Ga}$ ) were determined. The results for the air-dried samples are summarised in Table 2.

It can be seen from Table 2 that, as a function of the processing conditions, the parameter of uniplanar orientation ( $O_{gm}$ ) varies more strongly than ( $O_{gt}$ ) in a transverse direction. The strongest variation is found for the axial chain orientation ( $O_{Ga}$ ). For the sake of comparison, the corresponding parameters for a viscose sample are also given.

### 3. Wide Angle X-Ray Diffraction (WAXS)

WAXS investigations were performed in conventional manner with a wide angle X-ray diffractometer. From the corrected scattering curves of isotropised samples the degree of crystallinity ( $X_c$ ) and the lattice distortion parameter ( $k$ ) were calculated according to the Ruland-Vonk method. After peak separation, averaged lateral crystallite sizes ( $D_{hkl}$ ) were determined from the half-width of the peaks with the help of the Scherrer equation. Results for the air-dried samples are summarised in Table 3. The variation in degree of crystallinity as a function of processing conditions is relatively low ( $36-41^\circ$ ) for the present cellulose film. On the otherhand, the crystallinity of the conventional viscose casing is higher (about  $45^\circ$ ). The latteral crystalline sizes do not show

significant differences. Again, the values for the viscose sample are higher.

#### 4. Small Angle X-Ray Investigations (SAXS)

SAXS investigations were performed using a Kratky camera with a position sensitive linear detector. According to the Porod scattering theory, from the corrected scattering curves in absolute units, the volume fraction ( $W_v$ ) of the pores in colloidal dimensions, and a measure of the void diameter ( $I_v$ ) (cord main intersection length) as well as the internal surface ( $O_{sp}$ ) were calculated.

Table 4 shows the results of the SAXS investigations of dried and rewetted samples. It should be noted that the SAXS method records pores in colloidal dimensions (1 to about 100nm) only. Pore volume, average pore size and specific internal surface of the dried samples 3 and 4 do not differ significantly. After storage of these samples in water and careful drying by means of a solvent exchange procedure, pore volume and internal surface increase dramatically. This is more the case for sample 4 than for sample 3. For comparison, the effect is not present in viscose casings, and on the contrary pore volume and internal surface tend to decrease following such treatment.

Permeability

For selected samples from the experimental program, permeability measurements were carried out for which the results are shown in Table 5. Permeability is measured using a solution of  $K_3Fe(CN)_6$ . This shows that permeability for the NMMO casings of the present invention are higher than those for the comparison viscose casings.



TABLE 1

## Results of electron microscopy

Experiment	Precipitation bath temp. (°C)	cross-section	width of outer region (μm)	pore size (nm)			internal surface		
				outer region	middle	outer region	orientation	profile	bundle-dim. (nm)
1, never dried	20	asymmetrical	2.5...4	10...100	400...500	10...175			
1, dried	20	asymmetrical		5...45	5...45	5...150	none	embossed	15...70
2, never dried	10	symmetrical	2.5...3.5	10...60	10...100	10...60			
2, dried	10	symmetrical		5...30	5...50	5...30	none	flat	6.5...30
3, never dried	20	symmetrical	1.5...2.3	10...60	10...150	10...60			
3, dried	20	symmetrical			5...30		none	flat	6.5...30
4, never dried	10	symmetrical	1.5...2.5	10...60	10...100	10...60			
4, dried	10	symmetrical		5...30	5...25	5...30	none	flat	6.5...30
5, never dried	10	asymmetric	2.5	10...70	10...120	10...100			
5, dried	10						none	flat	6.5...30
6, never dried	20	asymmetric	1.5...2.6	10...120	10...350	10...80			
6, dried	20						none	embossed	15...70
7, never dried	10	asymmetric	2.0...4.0	10...60	10...60	10...200			
7, dried	10						none	flat	6.5...30
8, never dried	20	asymmetric	2.5...3.0	10...100	10...200	10...175			
8, dried	20						none	flat	15...50
14, never dried	10	asymmetric	0.5 1.0	10...60	10...100	10...100			
14, dried	10						none	flat	15...30
VISCOSE CASING		symmetrical		spindle-like voids a = 5...150, b = 300...750			strong in M-direction	w-shaped warplings, grooves	

TABLE 2

Oriental parameters from X-ray pole figure investigations

Sample dried	FWHM <sub>M</sub> [degree]	Uniplanar OG <sub>M</sub>	orientation FWHM <sub>T</sub> [degree]	OG <sub>T</sub>	Axial chain orientat. FWHM <sub>A</sub> [degree]	OG <sub>A</sub>
1	45.3	0.75	42.9	0.76	no orienta.	0
2	33.9	0.81	41.2	0.77	55	0.69
3	40.2	0.78	39.4	0.78	59	0.67
4	36.7	0.80	42.7	0.76	86	0.52
5	41.5	0.77	40.3	0.78	no orienta.	0
6	49.3	0.73	44.5	0.75	64	0.64
7	44.3	0.75	43.0	0.76	85	0.53
8	45.3	0.75	44.5	0.75	55	0.69
14	37.2	0.79	43.0	0.76	61	0.66
VISCOSE CASING	29.5	0.84	39.0	0.78	70	0.61

FWHM - full width at half maximum; M, T and A - machine, transverse and azimuthal directions; OG - orientational parameters

TABLE 3

Degree of crystallinity and crystallite sizes of the air-dried samples as determined from X-ray investigations

Sample dried	$x_c$ [%]	$k \cdot 10^2$ [nm <sup>2</sup> ]	$D_{(hkl)}$ [nm]		
			$D_{(101)}$	$D_{(10-1)}$	$D_{(002)}$
V1	39	2.6	3.9	4.6	3.3
V2	41	2.3	3.9	4.3	3.1
V3	39	2.1	3.6	4.1	3.4
V4	39	2.5	3.6	4.2	3.3
V5	38	2.4	3.9	4.3	3.2
V6	37	2.5	3.7	4.3	3.5
V7	36	2.3	3.7	4.0	3.4
V8	41	2.2	3.6	4.3	3.4
V14	36	2.2	3.9	4.1	3.5
VISCOSE CASING	45	2.3	4.5	4.5	3.6

$x_c$ - degree of crystallinity,  $k$ - disorder parameter,  $D_{hkl}$ - crystallite dimensions

TABLE 4

Table contains the results of the SAXS investigations of the dried and rewetted samples. It should be considered that the SAXS method records pores in colloidal dimensions (1 to about 100 nm) only.

Sample	$w_v$ [%]	$l_v$ [nm]	$O_{sp}$ [m <sup>2</sup> /cm <sup>3</sup> ]
3, dried	0.04	2.4	0.8
3, rewetted	0.58	3.3	7.0
4, dried	0.05	2.1	0.9
4, rewetted	1.97	3.6	22.2
VISCOSE CASING DRIED	0.25	2.4	4.3
VISCOSE CASING REWETTED	0.11	2.0	2.0

$w_v$ - volume fraction of pores,  $l_v$ - averaged pore dimensions,  $O_{sp}$ - specific internal surface

TABLE 5

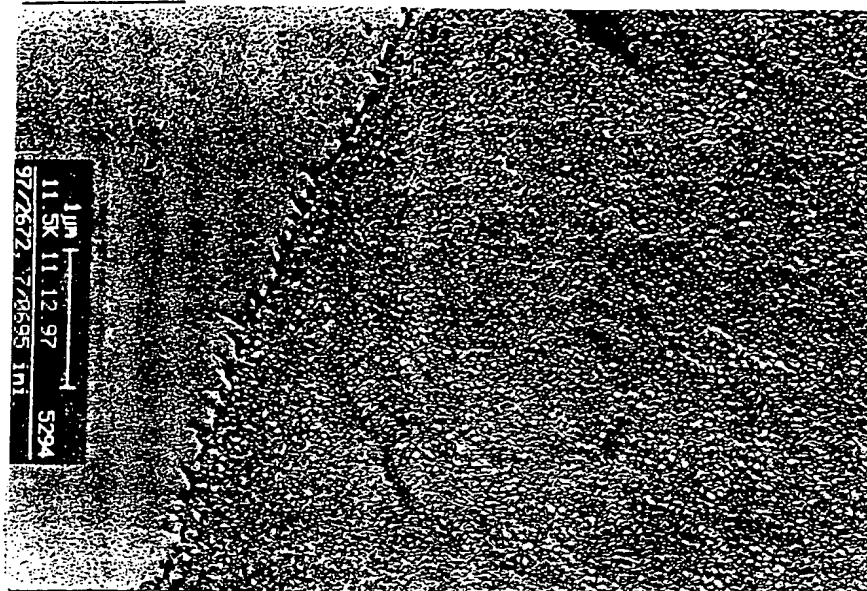
Permeability values of cellulose fibres (substance  $K_3Fe(CN)_6$ )

Experiment	permeation value (mg $\mu$ m ml/(min cm <sup>2</sup> g))
7	394
8	331
9	362
14	379
17	276
VISCOSE CASING	213

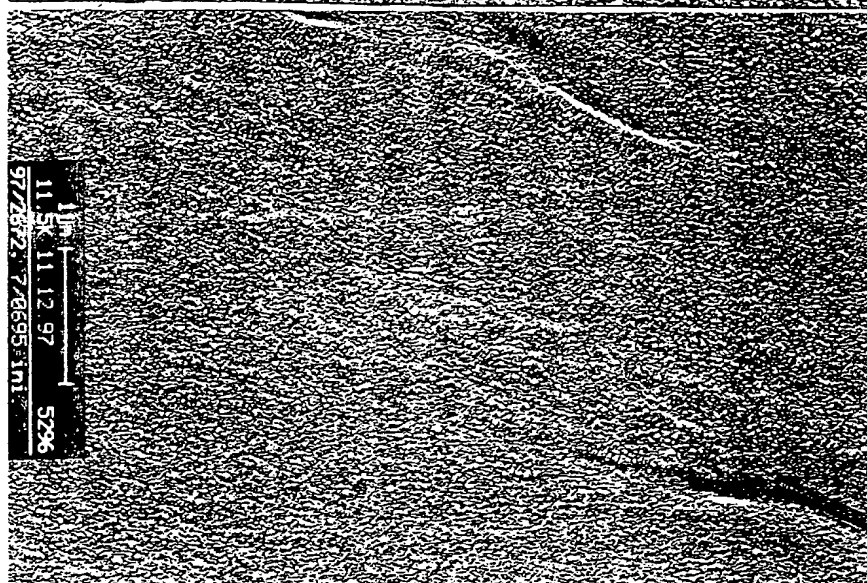
CLAIMS

1. An extruded cellulose film having a substantially uniform distribution of fine pores throughout its cross-section.
2. A cellulosic film as in claim 1 produced by extruding a dissolved cellulose solution in N Methyl Morpholine N-oxide mono hydrate.
3. A cellulosic film as in claim 1 with a permeability in the range 225-500 mg  $\mu$ m ml/min cm<sup>2</sup>g.
4. A cellulosic film as in claim 1 with a crystalline structure in the range 36-41% as measured with wide angle X-ray defraction.

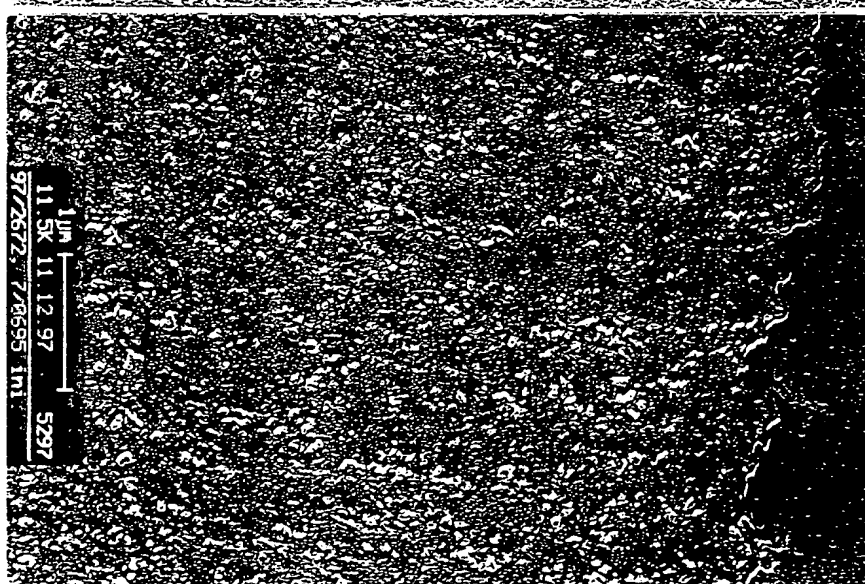
FIGURE 1



outer region



centre



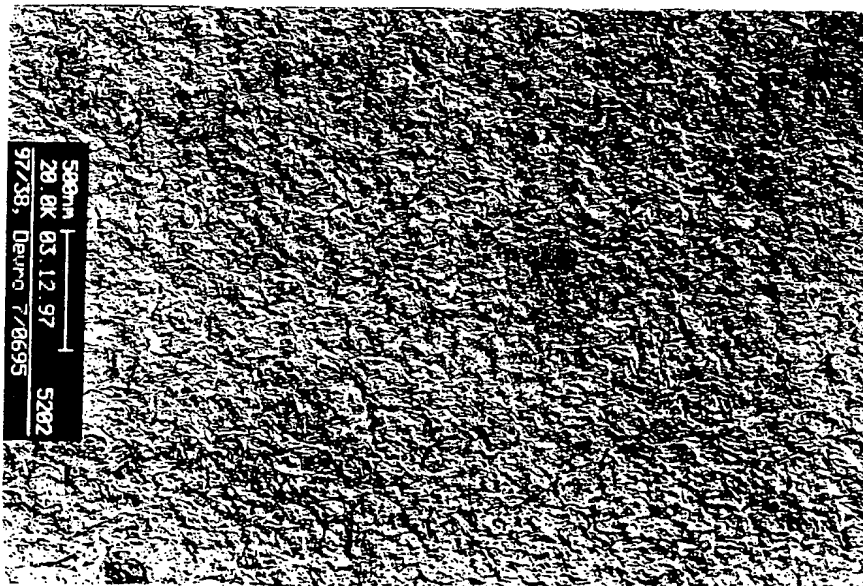
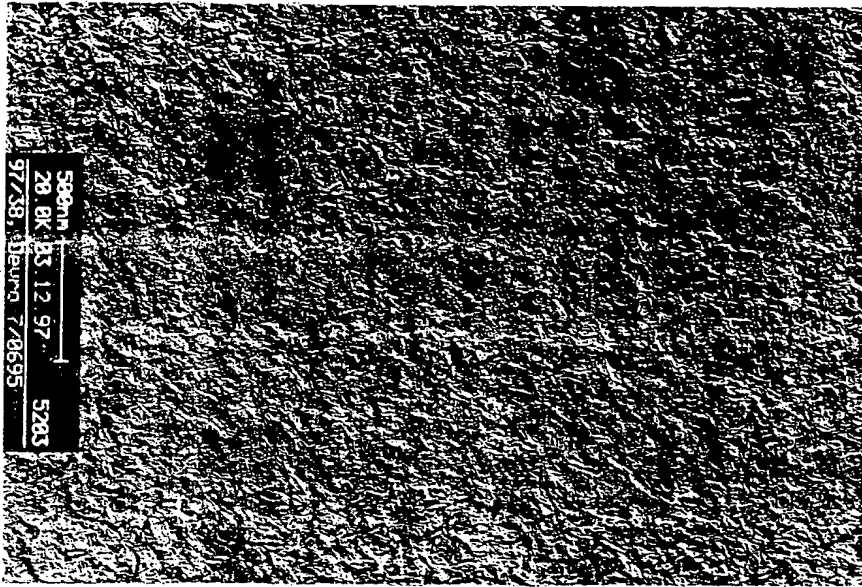
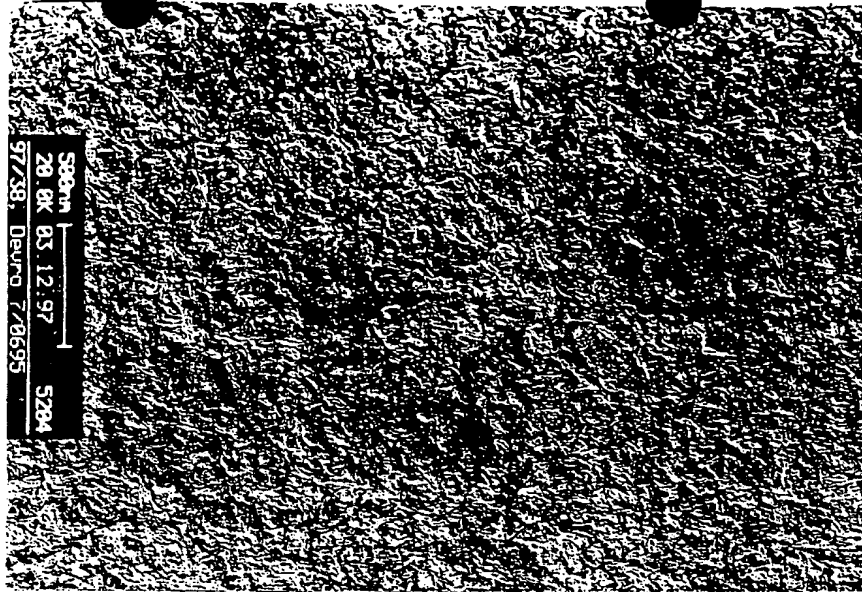
outer region

Cross sectional morphology of never dried sample 7





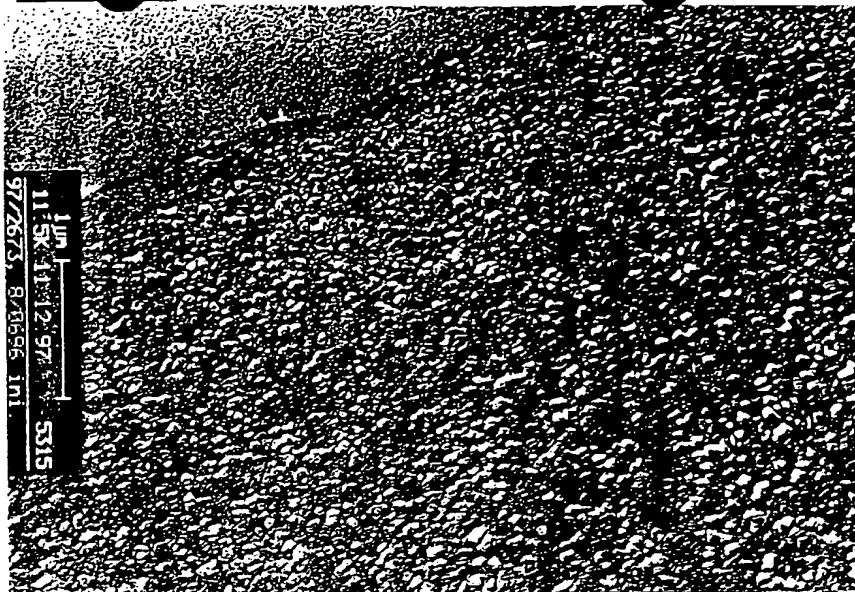
FIGURE 2



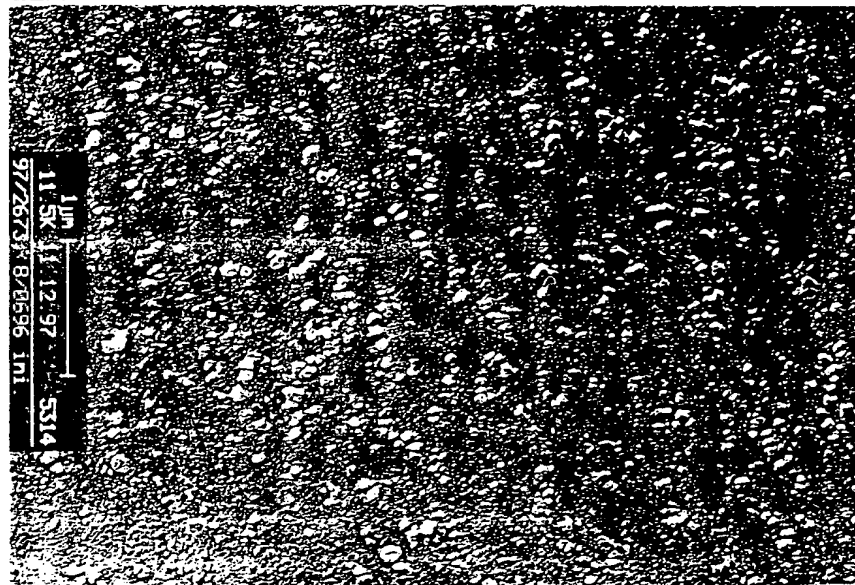
Internal surface of sample 7



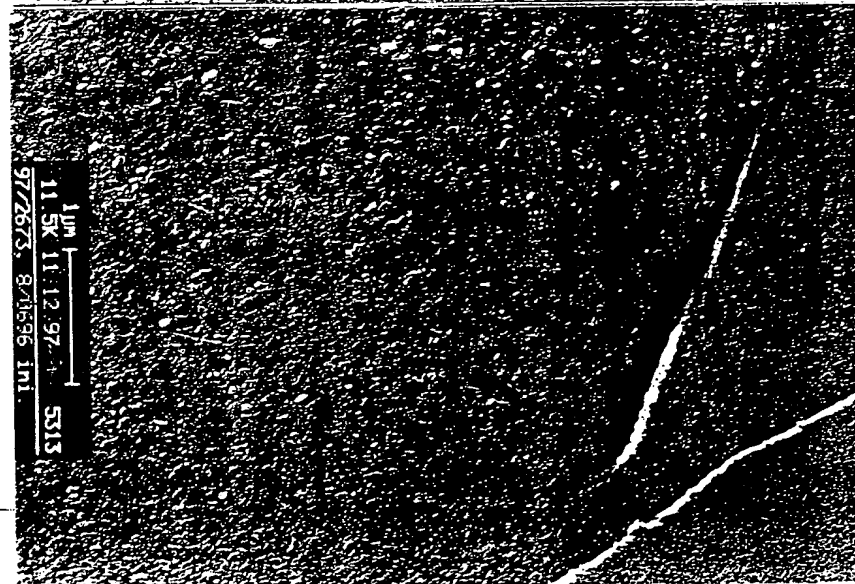
FIGURE 3



outer region



centre

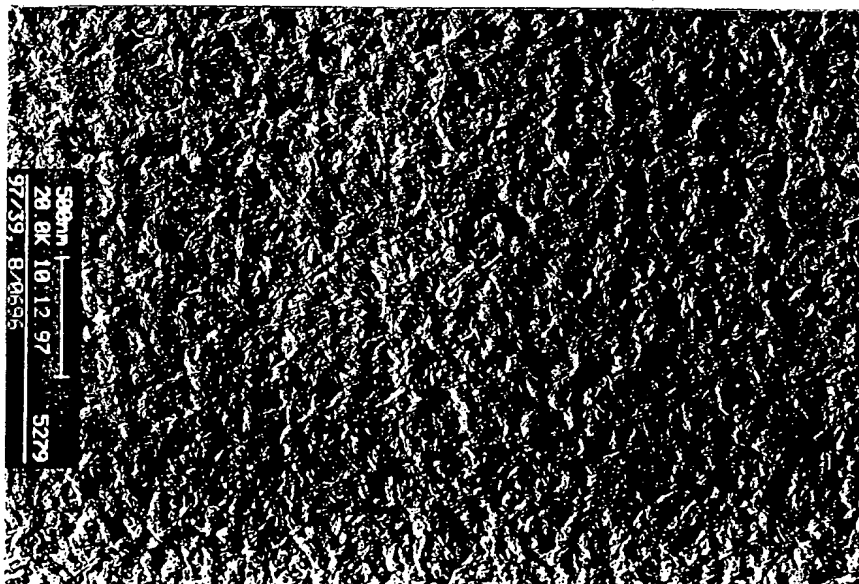
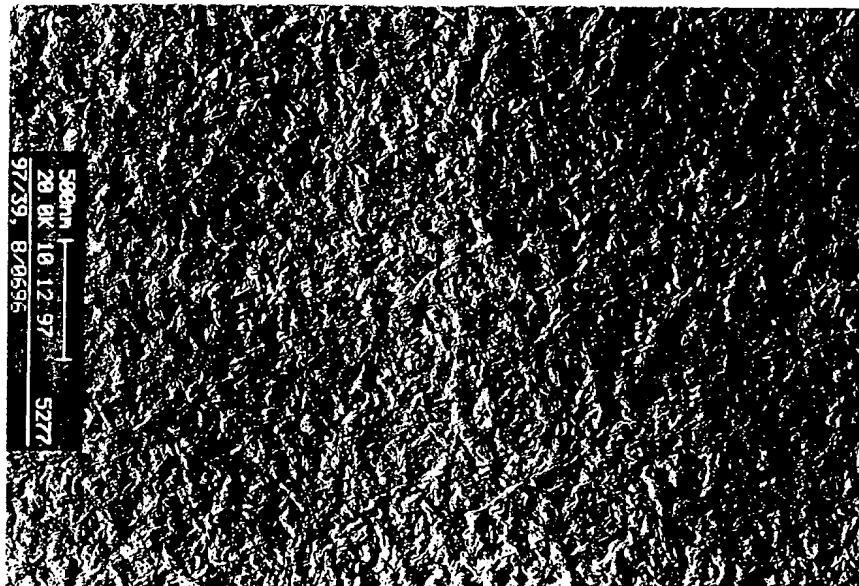


outer region

Cross sectional morphology of never dried sample 8



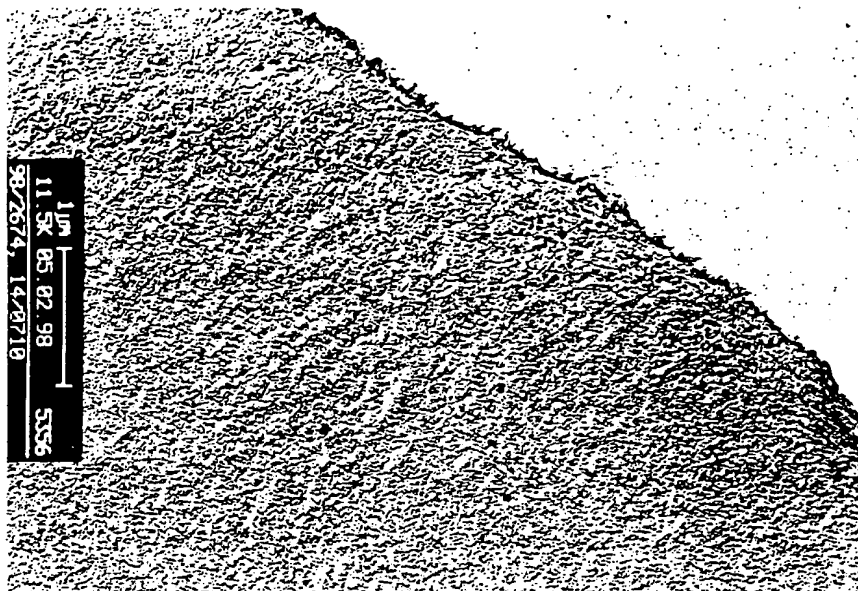
FIGURE 4



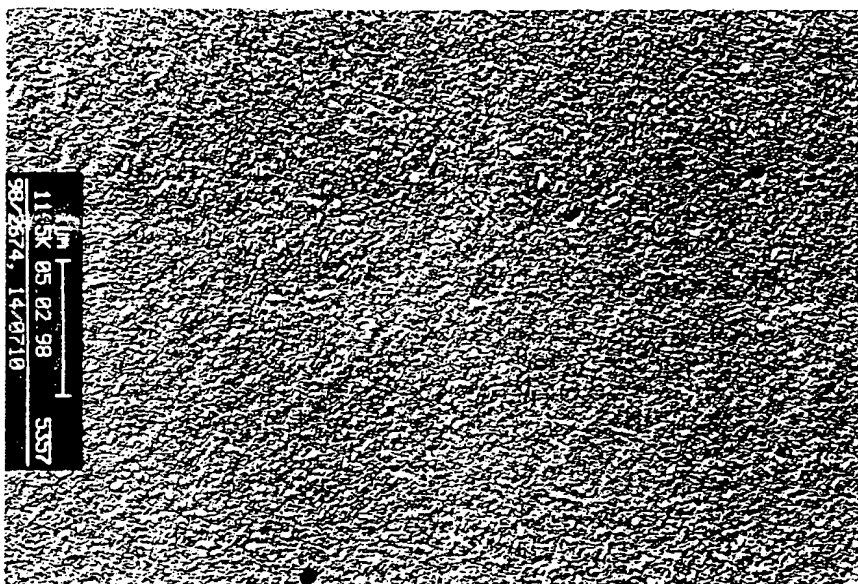
Internal surface of sample 8



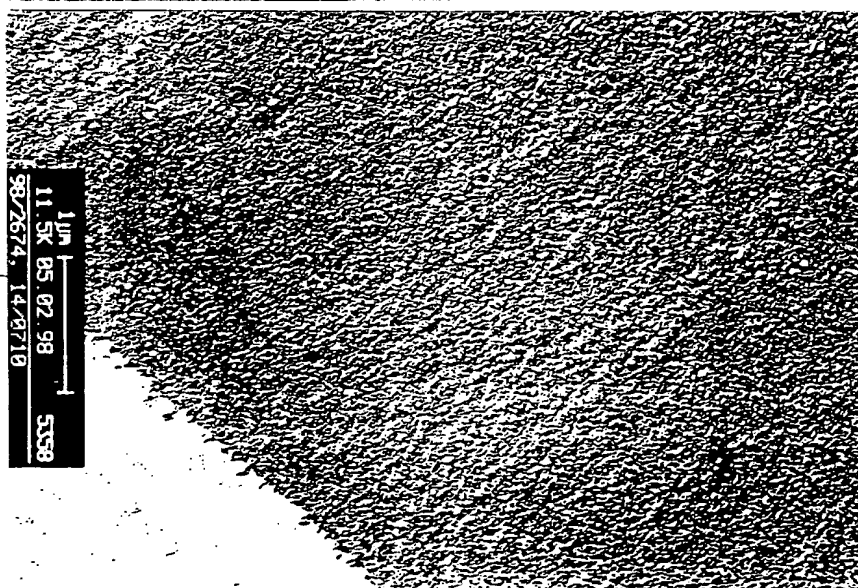
FIGURE 5



outer region



centre



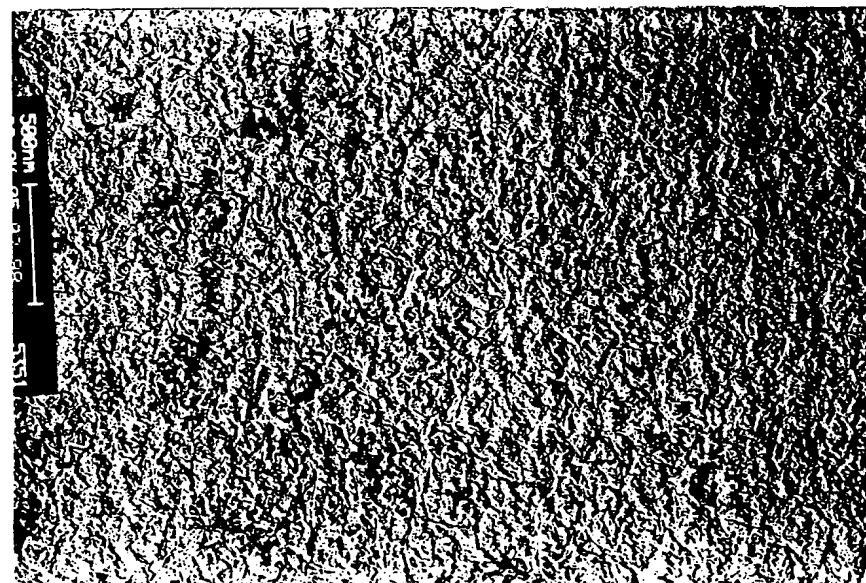
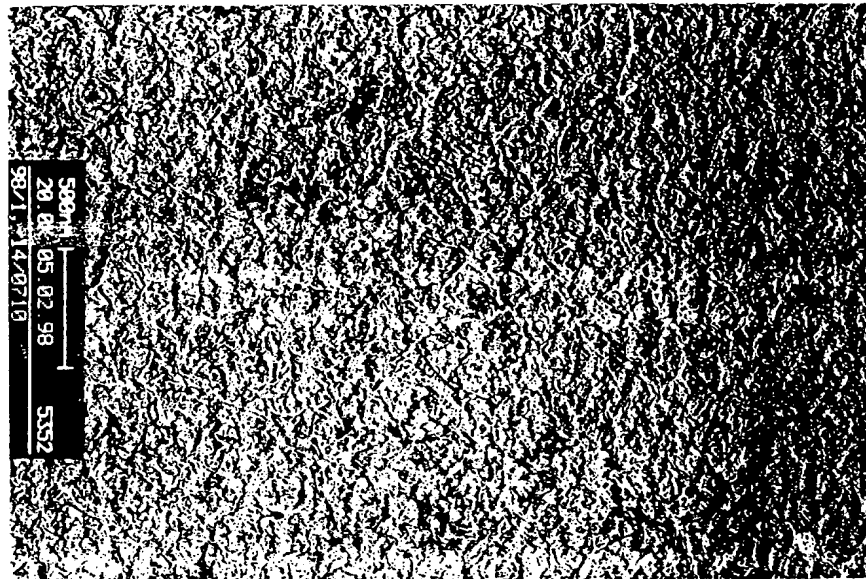
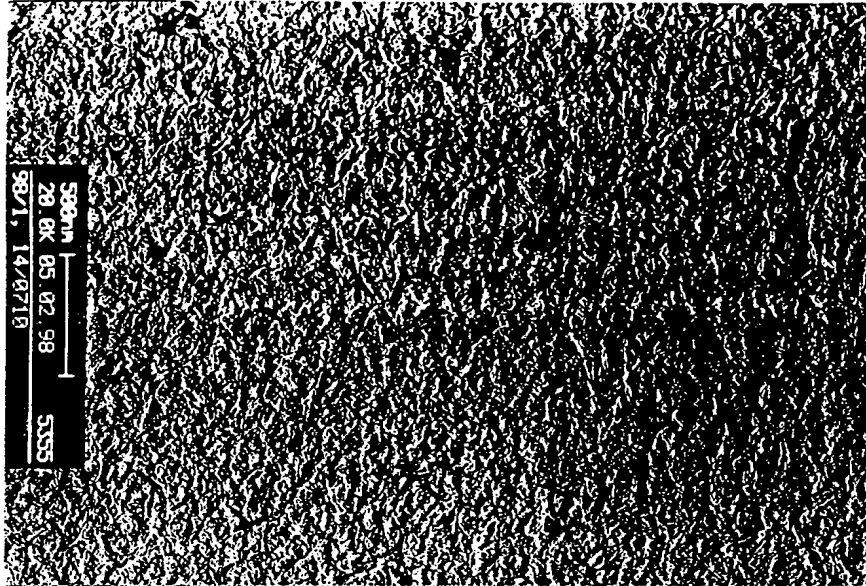
outer region

Cross sectional morphology of never dried sample 14





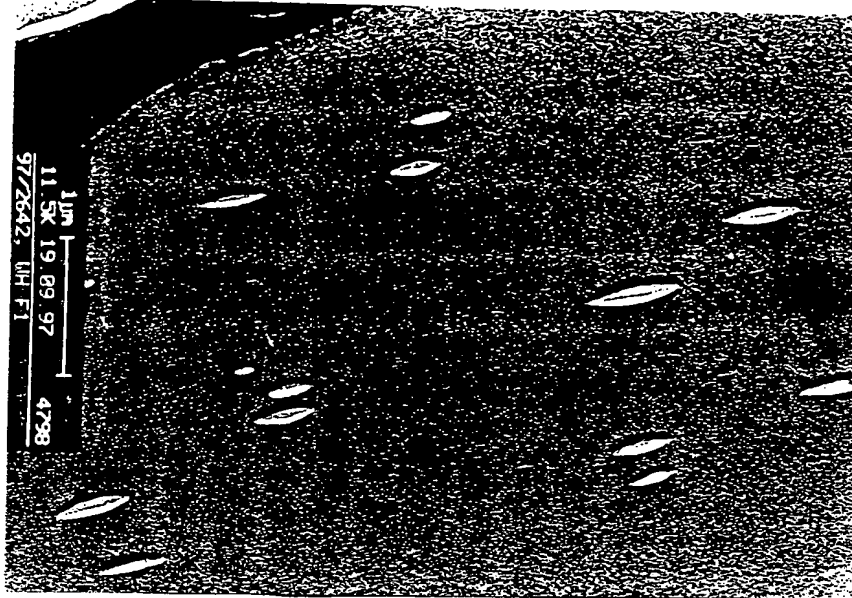
FIGURE



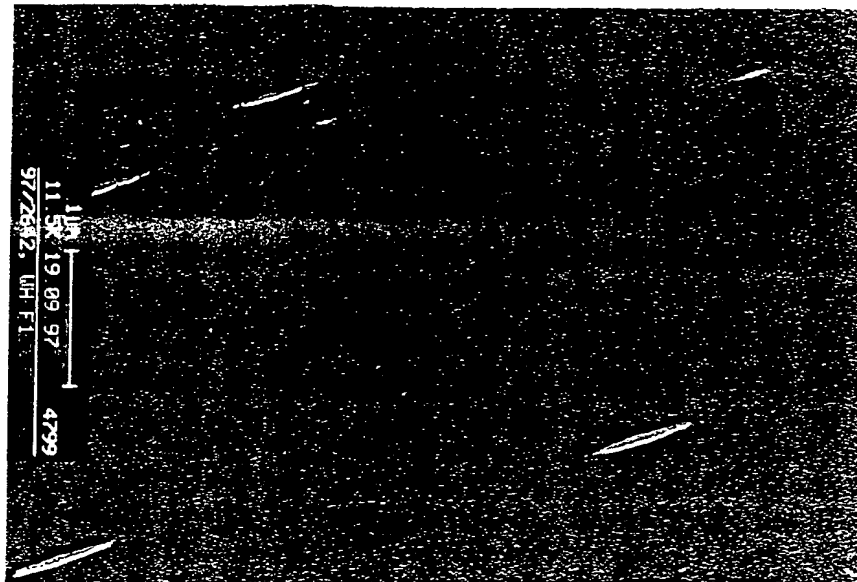
Internal surface of sample 14



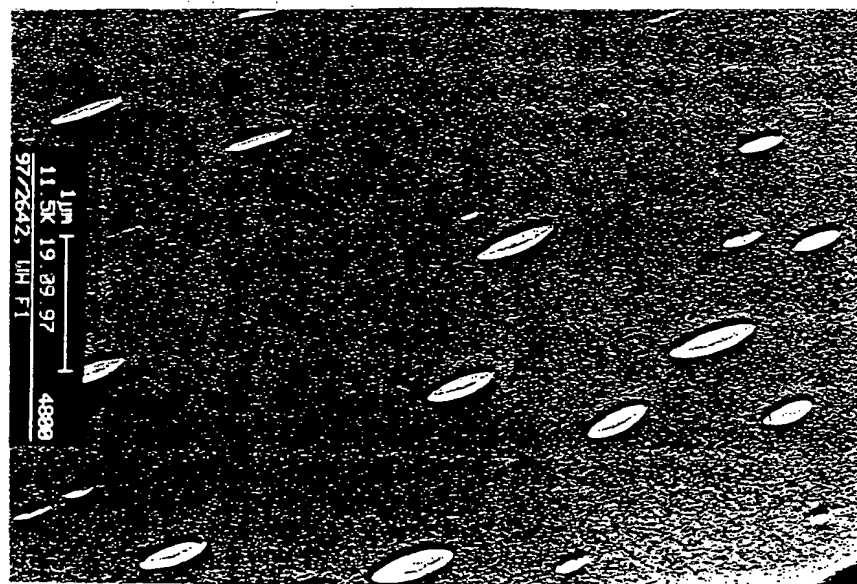
FIGURE 7



outer region



centre



outer region

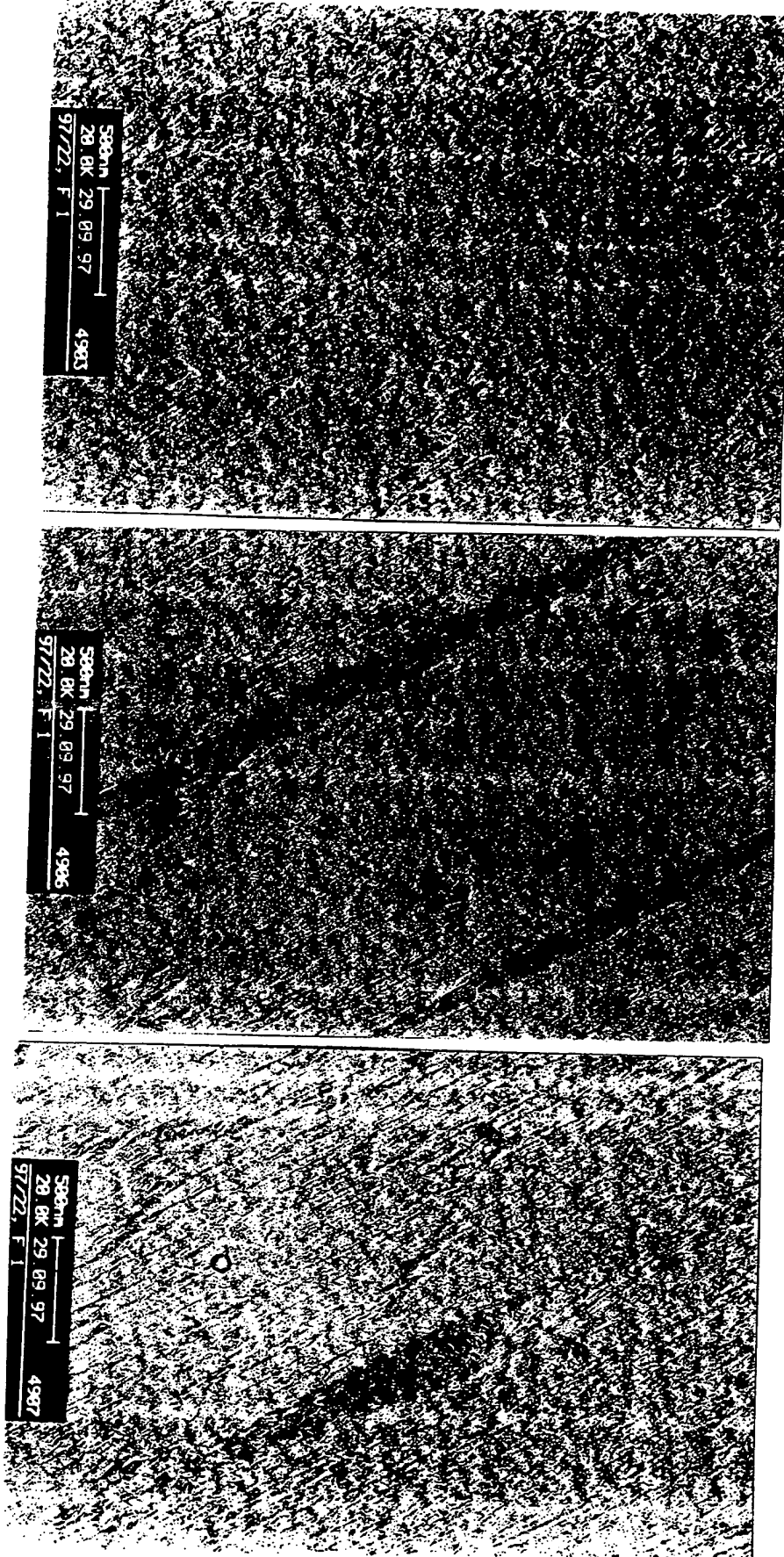
Cross sectional morphology of Lommel Standard code 02321o, rewetted



100-1000



FIGURE 8



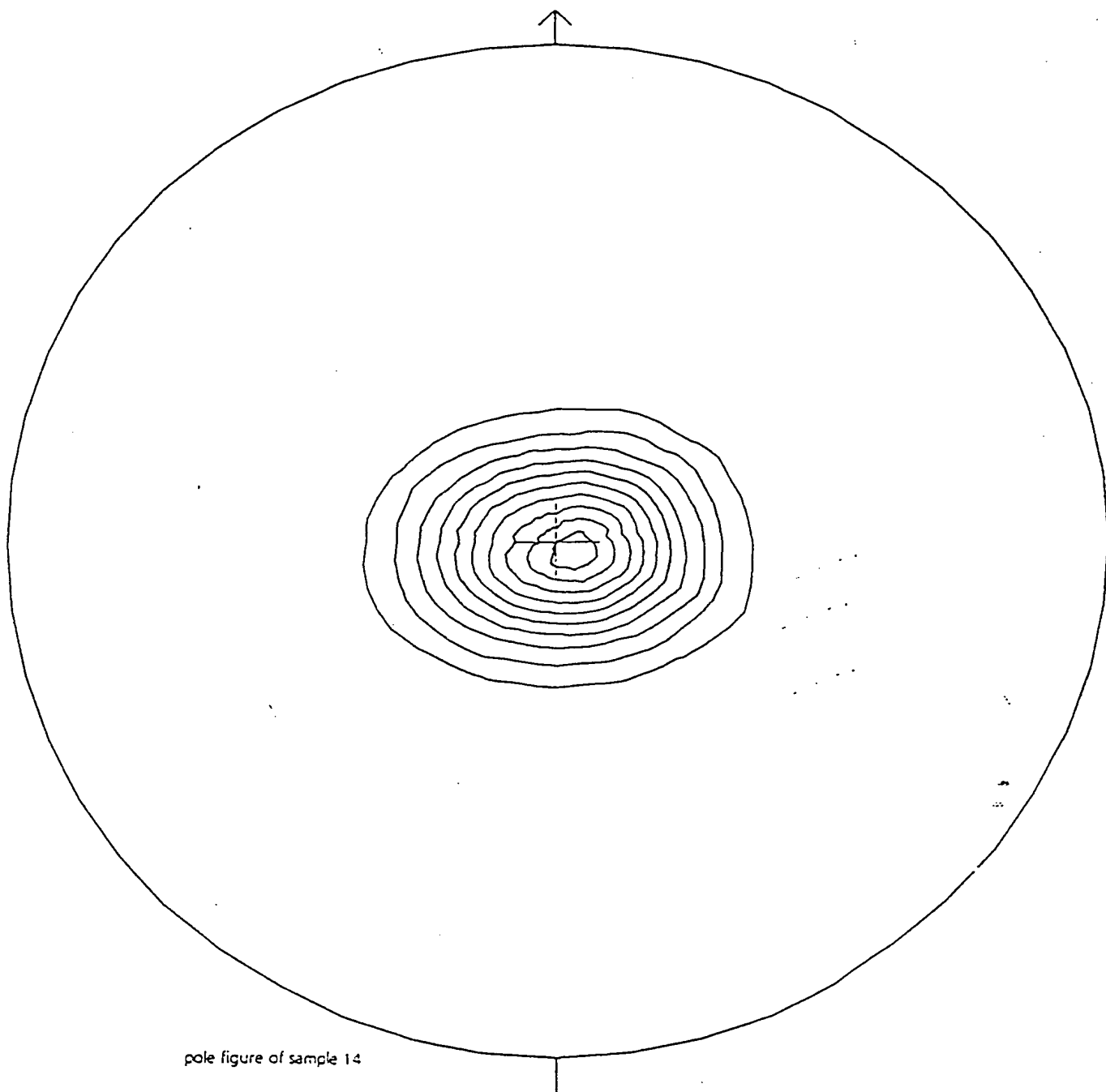
Internal surface of Lommel Standard code 023210



FIGURE 9

POLE FIGURE

0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4.50 5.00



PT/GB94/03439

18/10/99<sup>10</sup>

Cruikshank + Fairweather